Hydrochemistry, a tool for understanding karst groundwater flows

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ABSTRACT
Karst is a highly heterogeneous medium (i.e. properties vary from one point to another one), and can be studied by variations of water chemical composition, which reflect in space and time differences in origin (runoff on impervious media, diffuse seepage, inflows from evaporites…) or residence time throughout the various aquifer compartments (soil, epikarst, vadose and saturated zones. This natural background is supplemented by anthropogenic inputs (domestic, urban or industrial wastes, leachates from agricultural soils and livestock by-products...).
Any natural (cave, chiasm) or artificial (tunnel, mine) penetrable gallery is a means of observation and sampling, at least of infiltration water, and sometimes of water from the saturated zone.
Several cave sites in Europe provide examples for understanding the behavior of karst flows, both through the vadose and the saturated zones.

Keywords: Cave – Hydrochemistry - Groundwater flow - Environmental tracers

1 - Introduction: natural *vs.* man-constructed underground voids

As the easiest access point to permanent flows throughout the whole karst system was the spring, which is the outlet of the saturated zone, the whole karst behavior (volume of reserves, regulation of the dry season's discharge…) has been assigned for decades to the saturated zone. Speleological observations joint to examination of man-constructed tunnels, enabled to observe, to sample and even to monitor groundwater flows, either in the vadose or in the saturated zones.
Artificial galleries (Fig. 1A) display the advantage in a random sampling of water flows without any bias due to the drainage pattern of cave network structure.
Conversely, a cave (Fig. 1B) provides a 'natural' sampling pattern in a hierarchical conduit network. This means that the cave, being an active conduit (or at least a palæoconduit), is more subjected to enable sampling flows from different permeability contexts, whilst tunnels are devoid of organized inner structure, and may miss for instance major fractures generally well connected to cave conduits or pathways.
Nevertheless, both types of underground voids are complementary and enable studying flows in the karst aquifer.

2 – Flow types

Depending on the gallery level and according to the piezometric groundwater level, different flow components can be observed in caves:

- 'vauclusian' deep flooded shafts typically drain the saturated zone, below the base level. They can be considered as representative of flow through the deep compartment of the karst aquifer, as much in terms of hydrodynamics than in terms of physical, chemical and isotopic contents. But of course, this terminal conduit is the unique collector that drains all flows merging towards the spring. This conduit does not drain only 'old' or 'pre-event' water during low water periods, but also a mixture between 'pre-event' and 'event' waters during flood periods. This does not mean that all water flowing in low waters can originate only from the low permeability blocks of the saturated zone, a part of this 'reserve' water being permanently in transit through the vadose zone;

- in the case of 'jurassian' springs, cave networks develop within the fluctuation zone that separates vadose from saturated zones. This type of cave is very interesting, enabling to observe both the saturated and unsaturated flows. Generally, the main underground brook at the floor of the cave or in the deepest part of the cave, displays the same mixture possibilities with infiltration water as the former case. But this cave type enables also sampling dripping water, from lateral fractures (or at roof), and from speleothems;
- caves entirely dug within the unsaturated karst can sample only this second flow type, except in the case of hydraulic loading episodes, when flood water is evacuated via dry caverns situated several, and sometimes even several tenths of meters above the spring level;
- very shallow caves allow to encounter flows draining the epikarstic aquifer.

According to their situation *vs.* groundwater level, caves enable to sample saturated flows, vadose flows or both, the nature of the unit drained being under control of the hydro-meteorological events: water inflows through the unsaturated zone sample always infiltration fluxes (more or less rapid), whilst water conduits through or at the surface of the saturated zone can convey either reserve water, from the saturated zone or not, or a mixture of pre-event and event water in flood periods.

3 – Interest of hydrochemical methods

Along its cycle, water passes through different media (Fig. 2, from Hunkeler & Mudry 2007). From atmosphere where rainfalls leach marine and continental aerosols, through soil where it leaches CO_2 and organic acids, and then through epikarst where carbonic acid is neutralized by carbonate dissolution, and below, through vadose and finally saturated zones where minerals dissolve with a slower kinetics, water acquires a chemical composition enabling to use it as a an environmental tracing. Environmental, also called natural tracing is based on interpretation of contrasts (in space), and/or variations (in time) of physical (temperature, turbidity, electrical conductivity, pH, Redox potential…), chemical (major and minor ions, natural organic matter…), isotopic (oxygen, hydrogen, carbon, nitrogen, sulfur, strontium…) or biological (bacteria, viruses, protozoa…) composition of water.
Water content carries a composite message which reflects its story through the different media that interpretation and deconvolution assignable to a compartment of the hydrosystem.

4 – Case study of the Sierra del Rey—Los Tajos karst aquifer (Southern Spain, Fig. 3)

Each sector of the Sierra del Rey–Los Tajos aquifer has a different pattern of hydrological functioning. Los Tajos sector presents a high degree of functional karstification in its unsaturated zone, as shown by the variability of hydrochemical responses of the overflow springs when precipitation events occur (Fig. 4, Mudarra et al, 2011; Mudarra 2012). The karst draining here favors rapid infiltration and the flow of rainwater toward the springs, which provokes a rapid decrease in electrical conductivity. On the contrary, the main Auta spring, which is responsible for draining the saturated zone, responds to rainfall more slowly and with a time lag. This is due to the existence of a low degree of functional karstification in the saturated zone, with a slow drainage and a high natural regulation capacity. Both the saturated and unsaturated zones participate in the hydrological functioning of the Los Tajos system, but almost totally independently of each other. On the other hand, the Sierra del Rey springs respond to precipitation with rapid, severe hydrochemical variations, within 1 day. In this case, the springs drain a sector of the aquifer with a high degree of functional karstification, both in the saturated and in the unsaturated zones, and both are of similar participation in the hydrogeological functioning of the system.

5 – Case studies of accesses to the unsaturated zone: Nerja cave (Southern Spain) and LSBB gallery (Southern France)

Nerja cave is a shallow cave situated in the South-Spanish Mediterranean coast. Completely ubicated in the epikarst, this cave is a privileged site for sampling infiltration water below speleothems. Despite the thin limestone cover (only 35 m), a significant lag (Fig. 5) is observed after the rainfall: 8 months in normal period, falling to 2 months in exceptionally rainy period.
The LSBB is a previous military 4-km gallery intersecting vadose vertical water flows below the Vaucluse plateau. Several water inflows are intersected and enable sampling (Emblanch et al., 2011). Figure 6 displays the variability of magnesium, indicating residence time in this vadose zone, and Total Organic Carbon, characteristic of short transits through the unsaturated zone. Indeed, magnesium having slow dissolution kinetics separates water fallen several months ago (springs A and B) from water fallen several hours or days before (springs C, D and GAS). And Organic Carbon separates water infiltrated a very short time ago (springs C and GAS).

6 – Case study of the En Versenne-Fourbanne karst network (Eastern France)

The Fourbanne karst system (Charmoille, 2005, Gilli et al. 2012) includes (Fig. 7A) the Verne and Luxiol swallow holes, diffuse infiltration, and the passageways of the Fontenotte cave, which plunge into the saturated zone and lead to the karstic Fourbanne spring. The water's path was traced using fluorescein at the Verne loss, and this traced water has been sampled in Verne, Fontenotte, and Fourbanne. Nitrate concentrations of the traced mass appear in Figure 7B. Verne and Fontenotte display the same nitrate concentrations (as well as magnesium concentrations), showing the absence of mixing of other water with the water from the swallow holes (pinpoint infiltration), between the swallow holes and the underground river. At the Fourbanne spring, on the other hand, this localized infiltrated water is mixed with water of different composition (diffuse infiltration and/or saturated zone), with a higher magnesium concentration - larger residence time in the same limestone - and a lower nitrate concentration, less influenced by leaching from agricultural land (Fig. 7B).

7 – Conclusion

Underground cavities, cave networks as well as man-constructed tunnels are exceptional structures enabling sampling of water inflows. Understanding the karst behavior requires the knowledge of interaction between rapid flow in conduits and slow flow in microfissured blocks. Hydrochemistry appears as a very powerful tool to separate these origins. Hydrogeologists and cavers must work together in this task in the future.

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Figure 1: natural *vs* man-constructed gallery

A: Example of natural cave network: the Gour cave, Jura Mountains, Eastern France (after CDS 25, 1991)

B: Example of man-constructed gallery : the Galerie de la Mer, Gardanne, Southern France (after Hadadou et al. 2003)

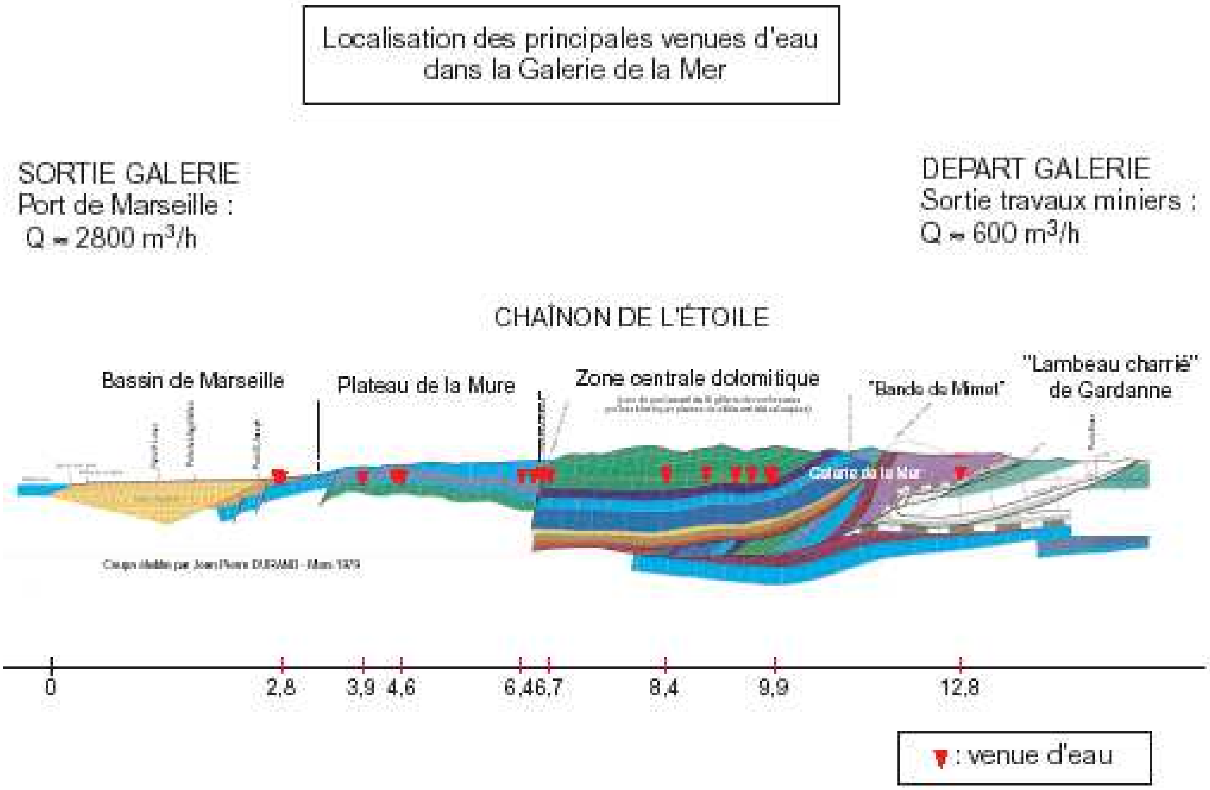


Figure 2: Factors influencing the hydrochemical parameters (Hunkeler & Mudry, 2007)

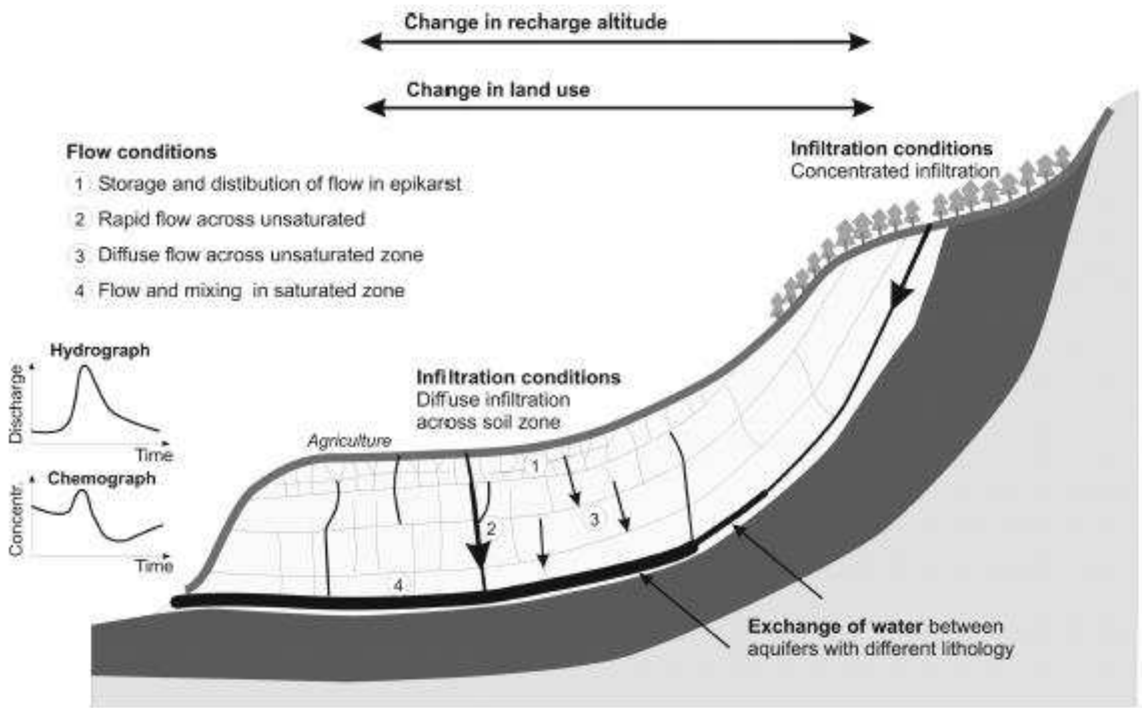


Figure 3: Sketches of the hydrogeological functioning of the systems drained by the springs (after Mudarra et al. 2011, and Mudarra 2012)

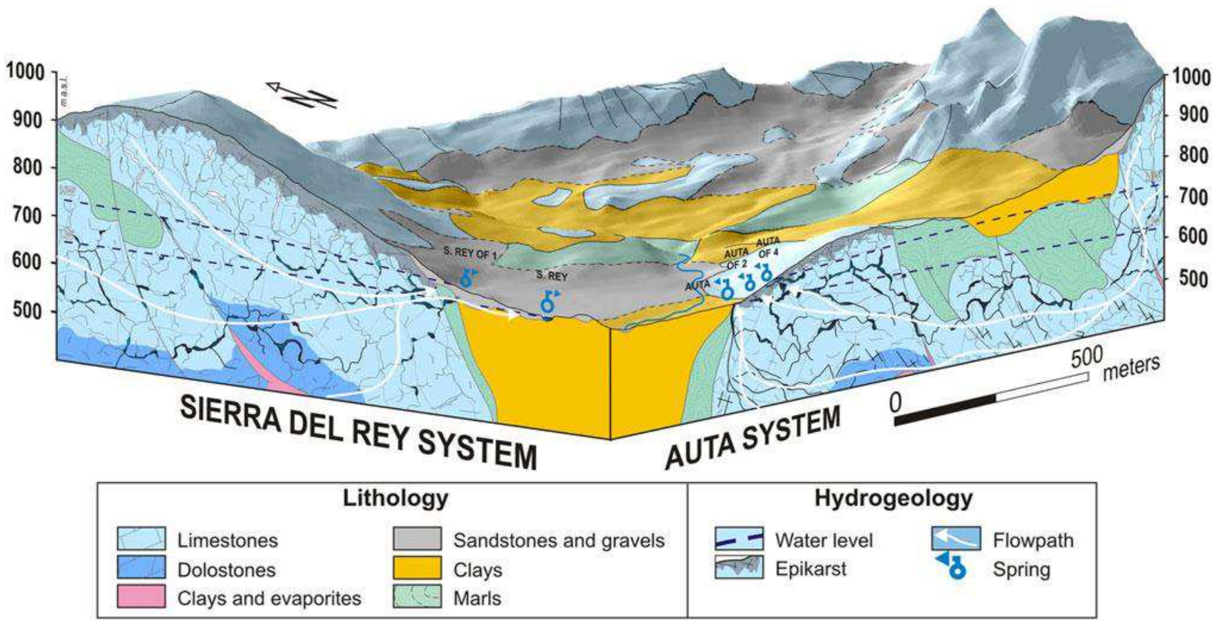


Figure 4: Box plots showing mean, maximum, minimum, percentiles 05, 25, 75 and 95 for electrical conductivity (EC), Temperature, Alkalinity, Mg^{2+}, pCO_2 , TOC and NO_3^- for each spring (Mudarra et al., 2011)

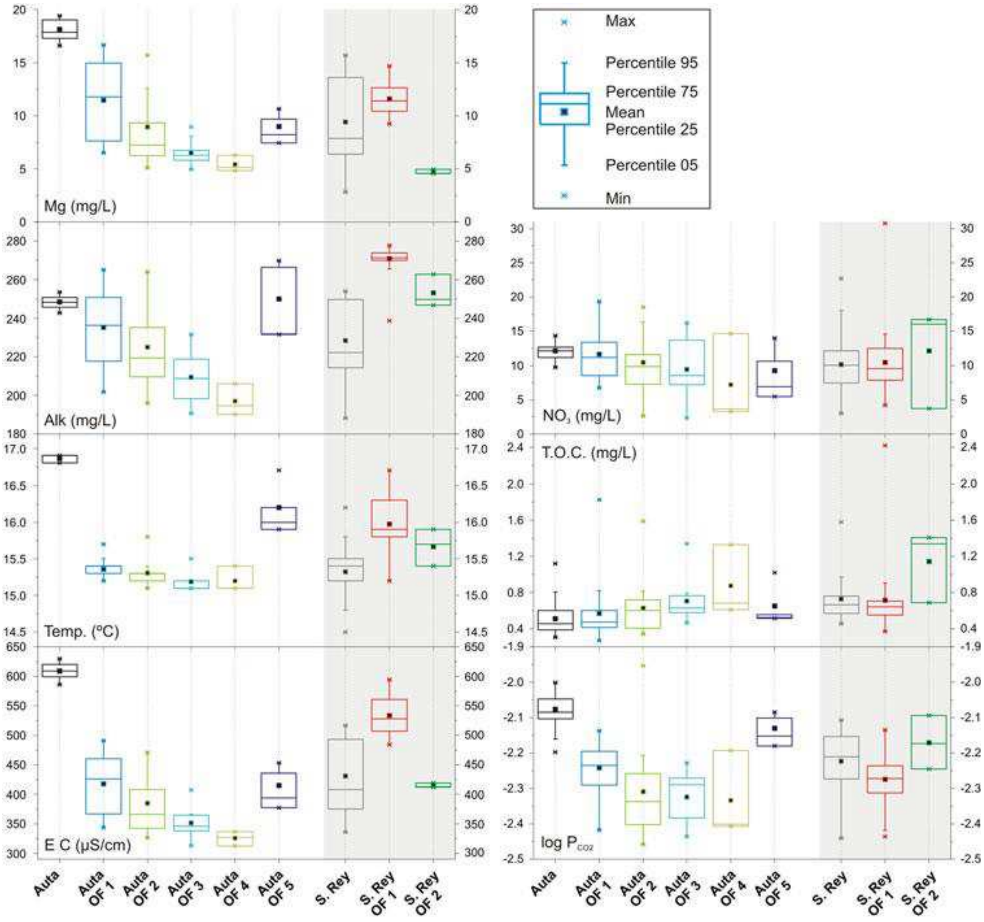


Figure 5: Fluxes of 18O stored through the unsaturated zone of the Nerja Cave (Southern Spain, after Carrasco et al, 2006) 1: normal flow, 2: rapid flow

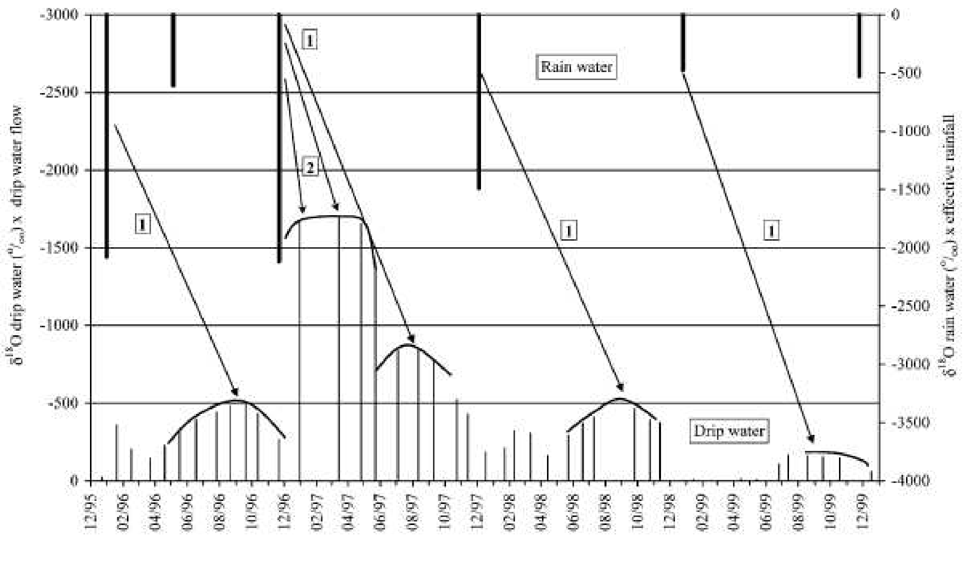


Figure 6: concentrations of Magnesium (residence time tracer) and Total Organic Carbon (soil tracer) in the Low Noise Underground Laboratory (LSBB Rustrel, France, after Emblanch et al. 2011)

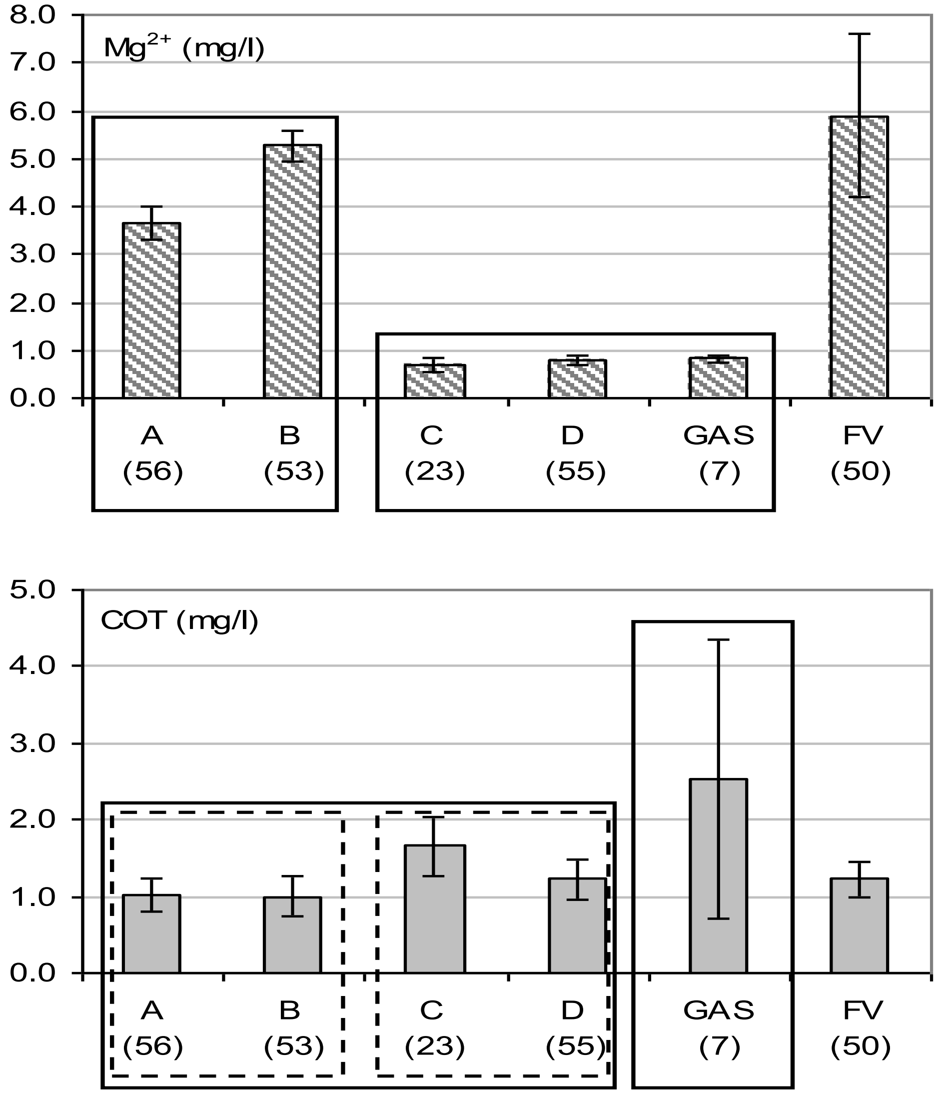
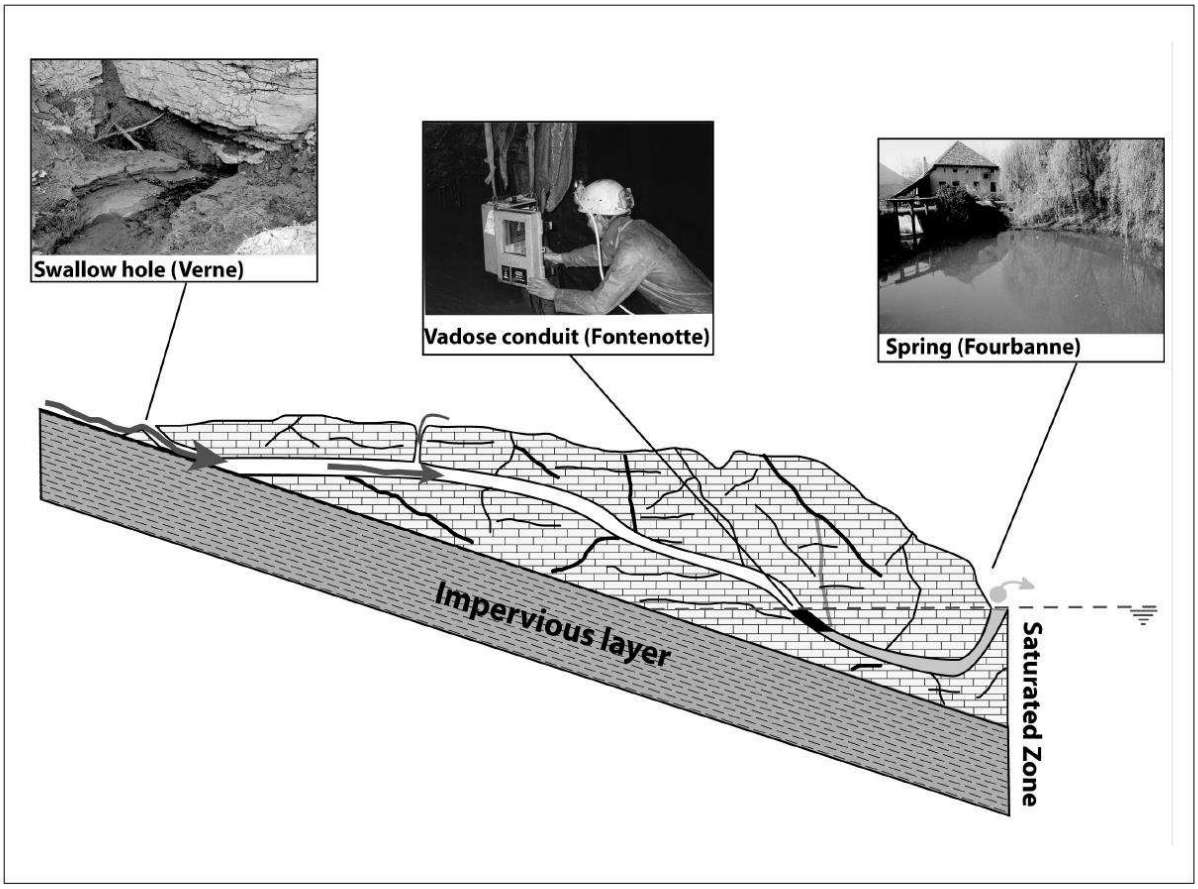


Figure 7: 3 monitoring spots in the Fourbanne karst hydrosystem. (after Charmoille, 2005)
A: organization 1: swallow hole; 2 vadose conduits down to the saturated zone (cave); 3: outlet



B: Dilution of nitrates from swallow holes by water from diffuse infiltration